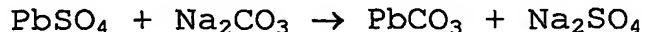


PROCESS FOR THE HIGH YIELD RECOVERY OF LEAD FROM SPENT
LEAD-ACID BATTERIES WITH REDUCED ASSOCIATED PRODUCTION
OF SLAG AND GASEOUS EMISSIONS

Secondary lead is recovered from the electrode slime recovered from end-of-life lead-acid batteries using pyrometallurgical processes operating at high temperature and in the presence of iron to reduce the furnace operating temperature to approximately 1100°C. These processes have a potentially high environmental impact, both as regards gaseous emissions and the large associated output of slag, which is classified as a hazardous material requiring disposal in special dumps. As far as gaseous emissions are concerned, the procedures adopted by lead recyclers make it possible to reduce and control these, although at a high cost, while the problem associated with the large output of associated slag persists. Conversion of the lead sulphate present in the electrode slime into carbonate through a "carbonatation" process is a technique which is well known among secondary lead producers. Processing lead carbonate instead of sulphate in furnaces brings advantages from the point of view of reducing gaseous emissions, the quantity of associated slag produced and energy consumption. The operating procedures adopted hitherto to effect the conversion of lead sulphate are those using sodium carbonate and sodium hydroxide, but these do not however succeed in complete desulphatation, or preventing dissolution of part of the lead salts.

The conversion of pure lead sulphate into carbonate takes place readily according to the reaction:



This reaction is displaced to the right because the solubility of the carbonate is $4.1 \cdot 10^{-6}$ moles/litre against $1.4 \cdot 10^{-4}$ moles/litre for the sulphate.

The actual composition of the slime, the crystallisation state of some compounds such as lead oxysulphate (lanarkite) and the presence of a grey material having the same composition as the slime and some metallic lead make this material little reactive to sodium carbonate with the result that desulphatation is only partial.

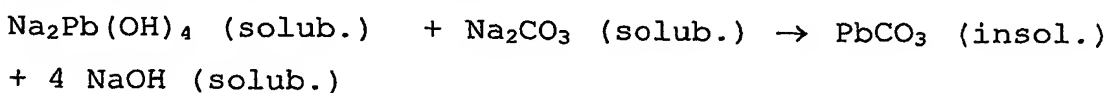
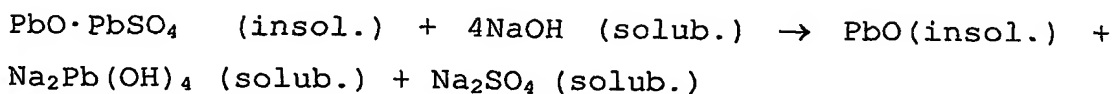
In a typical industrial desulphatation carried out using only sodium carbonate a maximum desulphatation yield of around 90% is in fact obtained. There is in fact a change from an initial sulphur content of approximately 5.5% in the slime to a final value of approximately 0.5 - 0.6%.

This only partial reduction in the sulphur content means that only limited advantage is derived from conversion pretreatment of the sulphate, in that in order to recover the lead it has hitherto been necessary to use iron, even if in a small quantity of 60-70%, with a corresponding reduction in the associated slag produced, but it is still necessary to operate using the same (high) temperatures as in the conventional process using a slime which has not been pretreated with sodium carbonate.

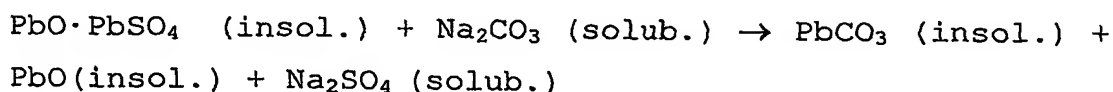
A method for virtually wholly desulphating the slime by reaction with an aqueous solution containing ammonium carbonate or alkali (sodium, ammonium, potassium) carbonates in addition to other substances which have the power to dissolve the insoluble lanarkite has now been found and is the subject of this invention.

Taking the example of sodium hydroxide into consideration, its decisive action during the desulphating reaction is due to the fact that being a much more alkaline substance than sodium carbonate it acts on the lanarkite and on the grey material through

a different mechanism, which is formally described by the following reactions:



In all:



This important result has been achieved in an efficient and economically acceptable way by subjecting the slime to treatment with an aqueous solution containing suitable proportions of sodium carbonate and sodium hydroxide. The action of the solution is assisted through a grinding action on the electrode slimes using shear and compression forces by the use of brushing, scraping and compressive mechanical means which make it possible to reduce the quantity of sodium hydroxides to levels such that soluble sodium plumbites do not form.

The effects of solution concentration and the stirring action are illustrated in the results shown in Table 1.

TABLE 1

| Slime g | Na ₂ CO ₃ g | NaOH g | Time Minutes | Temperature °C | Stirring | Insoluble residue % |
|------------|--------------------------------------|-----------|-----------------|-------------------|----------|------------------------|
| 100 | 25 | 3.75 | 90 | 70 | Grinding | 4-5.5 |
| 100 | 24 | 8.00 | 90 | 70 | Paddles | 3.41 |
| 100 | 24 | 7.00 | 90 | 70 | Paddles | 5.28 |
| 100 | 24 | 6.00 | 90 | 65 | Paddles | 9.00 |
| 100 | 24 | 0.00 | 90 | 65 | Paddles | 40.00 |

Using the method found a degree of desulphating of the slime which in practice can be regarded as being virtually total is obtained with extraordinarily short

treatment times and is nevertheless compatible with the productivity requirements of the overall lead recovery process, as the treatment time (average residence time) is generally between 60 and 90 minutes.

The treatment temperature may be between ambient temperature and the boiling point of the solution, preferably between 60 and 100°C.

Increasing the temperature reduces the contact time necessary for complete desulphatation, but does not substantially change the performance or desulphating yield achieved, which nevertheless remains virtually total.

The ratio by weight between the water in the solution and the slime lies between 0.6 and 5, preferably between 0.7 and 1.2.

The sodium carbonate present in the solution is the stoichiometric quantity appropriate for the sulphate levels present in the electrode slimes with an excess of between 0.01% and 10%. The sodium hydroxide is added in such a way that the carbonate/hydroxide ratio by weight lies between 6.4 and 5.5 so as to accelerate the desulphating reactions without plumbites being present in solution.

Working with a carbonate/hydroxide ratio of less than 5.5 the desulphating reaction takes place in shorter times and if soluble plumbites are present in solution at the end of treatment this is not prejudicial to the efficiency of the process because these can be easily precipitated out through the addition of a suitable quantity of sodium carbonate, sodium bicarbonate or CO_2 in order to return the carbonate/hydroxide ratio to a value of 5.5.

The mix of sodium carbonate and hydroxide is chosen simply on the basis of considerations of an economic nature, bearing in mind that a high percentage of sodium hydroxide speeds up the reaction, but it is then necessary to knock out the plumbites in solution.

The water/slime ratio may also be chosen in relation to the subsequent treatment separating the desulphated slime from the solution (normally by sedimentation, filtration and/or centrifuging). This does not apply any constraint on desulphating.

The water/slime/quantity of sodium carbonate ratio also depends on the subsequent treatment which it is intended to use to separate the sodium sulphate which forms as a result of the desulphating reaction described.

When it is intended to recover sodium sulphate decahydrate (Glauber's salt) from the solution by cooling, a water/slime ratio by weight of less than 1 will be chosen, while if it is intended to recover the sodium sulphate in anhydrous form the latter must remain in solution even after separation of the desulphated slime, given that it is recovered through total removal of the water present by known means such as evaporation under vacuum or spray drying in a flow of warm air.

With the slime desulphated by the method according to the invention, tests were performed on lead recovery using only carbon as a reducing agent, working at a temperature of 900-950°C for a time of between 2 and 3 hours.

The efficiency of lead recovery with reference to the weight of the non-desulphated dry slime was 71-72% in comparison with the maximum of 66% which can be obtained by known methods, while the maximum

theoretical yield is 72-73%, depending on the composition of the slime. The amount of slag formed essentially depends on substances present in the slime (carbon, adhesives, barium sulphate) and foreign substances brought in from the outer enclosures of the batteries (sand, grease), as well as residues of the auxiliaries and fluxes added to the furnace charge (sodium carbonate, glass, iron), and represents less than 12% of that produced during the conventional pyrometallurgical process for lead recovery.

Wholly similar results have been obtained with substances having the ability to dissolve lanarkite, such as:

amines, amides, MEA (monoethanolamine), DEA (diethanolamine), TEA (triethanolamine), tartaric acid and tartrates, citric acid and citrates, glycolic acid, gluconates, alkali and ammonium acetates, alkali and ammonium nitrates, ammonia, EDTA and other complexing agents, and with ammonium carbonate alone.

The invention is more specifically defined in the examples provided, which are not intended to be exhaustive as regards the invention and the appended claims.

EXAMPLES

Example 1

100 kg of electrode slimes were charged into a cylindrical mill reactor and suspended in a solution comprising 100 kg of water, 24 kg of 99% pure sodium carbonate and 3 kg of 99.5% pure sodium hydroxide. The suspension was heated to a temperature of 70°C and held at that temperature for 90 minutes. At the same time the solid part of the suspension was subjected to a strong compression and shearing force through rotating

brushes brushing against the inside walls of the reactor. At the end of the reaction the solid part of the suspension was separated out from the suspension and on analysis was found to have a total sulphur content of less than 0.06%.

The same desulphating experiment was repeated with sufficient quantities to charge an industrial furnace and a charge of 14 tons of desulphated slime with a residual moisture content of 30%, to which 0.5 tons of carbon, 0.2 tons of sodium carbonate and 0.1 tons of glass were added, produced a yield of 7,320 kg of lead metal accompanied by approximately 0.4 tons of slag with a lead content of less than 10%.

Example 2

100 kg of electrode slime was charged into a cylindrical reactor with a paddle stirrer and suspended in a solution comprising 100 kg of water, 24 kg of 99% pure sodium carbonate and 8 kg of 99.5% pure sodium hydroxide. The suspension was heated to a temperature of 70°C and held at that temperature for 90 minutes. Again in this case the grinding action was applied throughout the duration of the test. At the end of the reaction the solid part of the suspension was separated out from the and on analysis was found to have a total sulphur content of less than 0.04%.

Example 3

100 kg of electrode slime were charged into the same cylindrical reactor as in example no. 1 and suspended in a solution comprising 100 kg of water, 24 kg of 99% pure sodium carbonate and 5 kg of urea. The suspension was heated to a temperature of 75°C and held at that temperature for 90 minutes. Again in this case the grinding action was maintained throughout the duration of the test. At the end of the reaction the solid part

of the suspension was separated out and on analysis was found to have a total sulphur content of less than 0.09%.

Example 4

100 kg of electrode slime was charged into the same cylindrical reactor as in example no. 1 and suspended in a solution comprising 100 kg of water, 24 kg of 99% pure sodium carbonate and 6 kg of monoethanolamine. The suspension was heated to a temperature of 70°C and held at that temperature for 90 minutes. Again in this case the grinding action was maintained throughout the duration of the test. At the end of the reaction the solid part of the suspension was separated out and on analysis was found to have a total sulphur content of less than 0.07%.

Example 5

100 kg of electrode slime was charged into the same cylindrical reactor as in example no. 1 and suspended in a solution comprising 100 kg of water and 22 kg of 99% pure ammonium carbonate. The suspension was heated to a temperature of 70°C and held at that temperature for 90 minutes. Again in this case the grinding action was maintained throughout the duration of the test. At the end of the reaction the solid part of the suspension was separated out and on analysis was found to have a total sulphur content of less than 0.07%. It was not necessary to add solvent of any kind in this case because the ammonium ion $(\text{NH}_4)^+$ has the power of complexing lanarkite.